THE

OSMOTIC PRESSURE OF MANNITE SOLUTIONS BETWEEN TEN AND FORTY DEGREES

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

BY

EDWIN LOUIS FREDERICK

BALTIMORE

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THE OSMOTIC PRESSURE OF MANNITE SOLUTIONS BETWEEN TEN AND FORTY DEGREES.

INTRODUCTION.

Van't Hoff in his paper, "The Rôle of Osmotic Pressure in the Analogy Between Solutions and Gases," first deduced thermodynamically the relations between the lowering of vapor pressure and the lowering of the freezing point by dissolved substances and the osmotic pressure of these solutions.[1]

Nernst in his book, "Theoretical Chemistry," deduces the following:[2]

Let us take a cylinder containing a solution and the pure solvent which are separated from each other by a semipermeable partition (allowing free passage to the water, but not to the dissolved substance) in the form of a piston. As the piston is raised or lowered water will enter or leave the solution, thereby causing a dilution or concentration of the solution. But if we imagine the piston removed, the solute will diffuse up into the pure solvent; therefore it necessarily follows that an upward pressure will be exerted on the piston, and the greater this pressure is, so much greater is the work which the solute can perform in its expansion: the amount of this work can be calculated from the product of the pressure and the volume through which the piston is displaced.

Now, suppose we remove a small quantity of the solvent from the solution by lowering the piston. The expenditure of work necessary for this amounts to Pdv, in which dv is the volume through which the piston is lowered. Let the quantity of solvent removed from the solution be dxg. mol. Now we can also remove the same quantity of solvent from the solution by means of isothermal distillation, and denoting by p and p^1 the respective vapor tensions of the pure solvent, and of the solution at the temperature T, the expenditure of work necessary is

$$d \times R \, T \ln \frac{p}{p'} \qquad (1)$$

[1]Zeit. Phys. Chemie., 1, 498.
[2]Theoretical Chemistry, p. 134.

Now, since the work must be the same in these two isothermal and reversible ways, therefore

$$P\,d\,v = d\,x\,R\,T\ln\frac{p}{p'}$$

$$P = \frac{dx}{dv}\,R\,T\ln\frac{p}{p'} \qquad (2)$$

Now, as the addition of dx mols of the pure solvent to a sufficiently dilute solution produces neither contraction nor dilution, dv is obviously equal to dx mols; therefore

$$d\,v = \frac{M_0}{S}\,d\,x \qquad (3)$$

From (2) and (3)

$$P = \frac{S}{M_0}\,R\,T\ln\frac{p}{p'}$$

In order to obtain P in atmospheres we must express volume of one mol of the solvent in litres and must write 0.0821 for R; therefore

$$P = \frac{0.0821\ T\ 1000\ S}{M_0}\ln\frac{p}{p'}\ \text{atms.} \qquad (4)$$

From this it can be seen that solutions of various substances in the same solvent, when they have the same vapor pressure, are isosmotic. "Therefore, it follows directly from this that solutions of the solvent which have the same freezing point must have the same osmotic pressure. For as the freezing point is that temperature at which the solid solvent, ice, and the solution are capable of existing together, it must also be the point at which the curves of the vapor pressures of the solution and of the solid solvent cut each other, where both have the same vapor pressure. For if we suppose, for example, that the vapor pressure of ice and that of the water solution were different at the freezing point, then a process of isothermal distillation would begin, by which equilibrium would be disturbed; equilibrium can only be stable when the vapor of the solvent over the solution and the solid is of the same density. Therefore, solutions of the same freezing point have equal vapor pressures, namely, that of the separated ice, and are isotonic."[1]

Now, the relation which exists between the lowering of the freezing point and the osmotic pressure of a solution can be

[1]Theoretical Chemistry, p. 137.

deduced by combining the equation for the molecular heat of sublimation with that for the heat of vaporization, λ, whence upon integration we get[1]

$$\ln \frac{p}{p'} = \frac{\sigma - \lambda}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \qquad (5)$$

From (4) and (5) we get

$$P = \frac{1000\ S\ .\ w\ t}{24.19\quad T_0} \text{ atms.} \qquad (6)$$

Where $w = \frac{\sigma - \lambda}{M}$ = heat of fusion of 1 gr. of the solvent expressed in gr. cal.; T_0 = fusing point; S = specific gravity and t denotes $T_0 - T$, the lowering of the freezing point and 24.19 is the factor to reduce cal. to litre atmospheres.

Thus, for an aqueous solution we have

$$P = \frac{1000 \text{ x } 79.6\ t}{24.19 \text{ x } 273} = 12.05\ t \text{ atms.}$$

where t equals $T_0 - T$ the lowering of the freezing point.

Thus by means of this equation we are able to calculate within a limited range of temperature, which includes the freezing point itself, the osmotic pressure of a solution whose lowering of the freezing point we know.

Let us take, for example, Cane Sugar and Glucose.

TABLE I.

DEPRESSION OF THE FREEZING POINTS OF WEIGHT-NORMAL SOLUTIONS.[2]

	CANE SUGAR.		GLUCOSE.	
Concentration.	*Depression.*	*Molecular Depression.*	*Depression.*	*Molecular Depression.*
	Degrees.	*Degrees.*	*Degrees.*	*Degrees.*
0.1	0.195	1.95	0.192	1.92
0.2	0.393	1.96	0.386	1.92
0.3	0.584	1.95	0.576	1.92
0.4	0.784	1.96	0.762	1.91
0.5	0.983	1.97	0.952	1.91
0.6	1.190	1.98	1.147	1.91
0.7	1.390	1.99	1.337	1.91
0.8	1.621	2.02	1.528	1.91
0.9	1.829	2.03	1.720	1.91
1.0	2.066	2.07	1.918	1.92

[1] *Ibid.*, p. 138.

[2] The Osmotic Pressure of Aqueous Solutions. Report on investigations made in the chemical laboratory of The Johns Hopkins University during the years 1899-1913, by H. N. Morse. Carnegie Institution of Washington. Publication 198.

TABLE II.

CANE SUGAR—WEIGHT-NORMAL CONCENTRATION.[1]

	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Temp.					*Ratio of Osmotic to Gas Pressure.*					
0°	(1.106)	1.061	1.061	1.060	1.069	1.077	1.083	1.093	1.104	1.115
5°	1.082	1.063	1.058	1.059	1.067	1.074	1.084	1.093	1.102	1.115
10°	1.082	1.060	1.059	1.060	1.066	1.073	1.083	1.092	1.102	1.113
15°	1.082	1.061	1.061	1.059	1.068	1.073	1.083	1.093	1.102	1.115
20°	1.084	1.062	1.060	1.060	1.067	1.073	1.084	1.093	1.103	1.115
25°	1.084	1.059	1.060	1.059	1.065	1.071	1.083	1.093	1.102	1.113
	(1.083)	(1.061)	(1.060)	(1.060)	(1.067)	(1.074)	(1.083)	(1.093)	(1.103)	(1.114)
30°	1.000	1.020	1.031	1.040	1.050	1.060	1.069	1.081	1.089	1.101
40°	1.003	1.011	1.024	1.038	1.046	1.054	1.059	1.067	1.076	1.085
50°	1.000	1.002	1.009	1.017	1.025	1.032	1.041	1.049	1.059	1.071
60°	1.000	1.001	0.999	1.000	1.006	1.015	1.020	1.027	1.033	1.044
70°	-----	-----	-----	-----	1.000	1.002	0.999	1.008	1.015	1.023
80°	-----	-----	-----	-----	-----	-----	-----	1.001	1.000	1.000
90°	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
100°	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----

[1]Carnegie Publication 198.

Thus from Table II we see that:

(1) In all solutions of cane sugar from 0.1 to 1.0 weight-normal, the ratio of the observed osmotic to the estimated gas pressure of the solute is constant for each concentration between 0° and 25°.

(2) This ratio exceeds unity in every instance. This suggests, of course, that the solution has become concentrated through a withdrawal of some of the solvent for the purpose of hydrating the solute.

(3) When the solutions of cane sugar are heated to a temperature above 25°, the ratios of the osmotic to gas pressure, which are all above unity, begin to decline. This decrease is relatively more rapid in dilute than in concentrated solutions.

(4) This decline in the ratios, which begins at a little above 25°, continues until at some temperature which is characteristic for each concentration it becomes unity; and there is considerable evidence that a ratio having once become unity at some temperature does not further decline at higher temperatures.

(5) Glucose solutions behave somewhat analogous to cane-sugar solutions, as is shown by Table III. At 0° the ratio of osmotic to gas pressure is greater than unity, which suggests hydration, but this ratio is the same in the case of glucose for all concentrations. At some temperature above 0°, but below 10°, this ratio begins to decline. At 10° half the difference between the observed ratio at 0° and unity has disappeared, but still the ratio is the same for all concentrations. At 25° and 30° the ratio is unity for all concentrations from 0.1 to 1.0 weight-normal.[1]

TABLE III.

GLUCOSE—WEIGHT-NORMAL CONCENTRATIONS.

	0.1	0.2	0.3	0.4	0.5
Temp.		*Ratio of Osmotic to Gas Pressure.*			
10°	1.035	1.030	1.027	1.030	1.031
30°	1.001	1.002	1.000	1.000	1.000
40°	1.001	1.001	1.001	0.999	1.000
50°	1.000	1.002	1.001	1.000	1.002
60°	1.002	-----	0.999	0.998	0.999

[1]Carnegie Publication 198.

	0.6	0.7	0.8	0.9	1.0
Temp.		*Ratio of Osmotic to Gas Pressure.*			
10°	1.033	1.033	1.032	1.030	1.031
30°	1.001	1.001	1.000	1.002	1.001
40°	1.001	1.000	0.999	1.001	1.000
50°	1.000	1.000	0.998	0.998	1.000
60°	-----	-----	-----	-----	-----

TABLE IV.

OSMOTIC PRESSURES OF CANE SUGAR CALCULATED FROM FREEZING POINTS (TABLE I) WITH THOSE DIRECTLY DETERMINED.[1]

	0°		5°		10°		15°	
Conc.	*Calc.*	*Det.*	*Calc.*	*Det.*	*Calc.*	*Det.*	*Calc.*	*Det.*
0.1	2.35	2.46	2.39	2.45	2.43	2.50	2.48	2.54
0.2	4.72	4.72	4.81	4.82	4.89	4.89	4.98	4.99
0.3	7.04	7.09	7.17	7.20	7.30	7.33	7.43	7.48
0.4	9.44	9.44	9.61	9.61	9.78	9.79	9.95	9.95
0.5	11.86	11.90	12.08	12.10	12.29	12.30	12.51	12.55
0.6	14.30	14.38	14.56	14.61	14.82	14.86	15.08	15.14
0.7	16.77	16.89	17.07	17.21	17.37	17.50	17.69	17.82
0.8	19.45	19.48	19.81	19.82	20.16	20.16	20.52	20.54
0.9	21.99	22.13	22.39	22.48	22.80	22.88	23.20	23.21
1.0	24.91	24.83	25.37	25.28	25.82	25.69	26.28	26.19

	20°		25°		30°		40°	
Conc.	*Calc.*	*Det.*	*Calc.*	*Det.*	*Calc.*	*Det.*	*Calc.*	*Det.*
0.1	2.52	2.59	2.56	2.63	2.61	2.47	2.69	2.56
0.2	5.06	5.06	5.15	5.15	5.24	5.04	5.41	5.16
0.3	7.56	7.61	7.69	7.73	7.82	7.65	8.07	7.84
0.4	10.13	10.14	10.30	10.30	10.47	10.30	10.82	10.60
0.5	12.73	12.75	12.94	12.94	13.16	12.98	13.60	13.36
0.6	15.35	15.39	15.61	15.63	15.87	15.71	16.40	16.15
0.7	17.99	18.13	18.30	18.44	18.61	18.50	19.23	18.93
0.8	20.88	20.91	21.23	21.25	21.59	21.38	22.30	21.80
0.9	23.60	23.72	24.01	24.13	24.41	24.23	25.22	24.74
1.0	26.74	26.64	27.20	27.05	27.66	27.22	28.57	27.70

	50°		60°		70°		80°	
Conc.	*Calc.*	*Det.*	*Calc.*	*Det.*	*Calc.*	*Det.*	*Calc.*	*Det.*
0.1	2.78	2.64	2.86	2.72	-----	-----	-----	-----
0.2	5.58	5.28	5.76	5.44	-----	-----	-----	-----
0.3	8.33	7.97	8.59	8.14	-----	-----	-----	-----
0.4	11.17	10.72	11.51	10.87	-----	-----	-----	-----
0.5	14.03	13.50	14.47	13.66	14.90	13.99	-----	-----
0.6	16.92	16.32	17.45	16.54	17.91	16.82	-----	-----
0.7	19.84	19.20	20.46	19.40	21.07	19.57	-----	-----
0.8	23.02	22.12	23.73	22.33	24.44	22.57	25.16	23.06
0.9	26.02	25.12	26.83	25.27	27.64	25.56	28.44	25.92
1.0	29.48	28.21	30.40	28.37	31.31	28.62	32.23	28.82

[1]Carnegie Publication 198.

Thus, from Table IV we see that the osmotic pressure of cane-sugar solutions up to and including 25° can be calculated from the observed abnormal depressions of the freezing points. But at higher temperatures this can not be done. They can be calculated, then, up to that temperature at which the ratio of osmotic to gas pressures which was constant but abnormally high begins to decline. In other words, up to 25° the osmotic pressures as compared with the theoretical gas pressures of the solute are abnormal to the same degree as the observed freezing point lowerings as compared with the theoretical lowering, but this is not true at higher temperatures. At those temperatures above 25° where the ratio of osmotic to gas pressures becomes constant and unity, we could calculate the osmotic pressure of the solution, not from the observed freezing point lowering, but from the theoretical depression, that is, a molecular depression of 1.85°.

In the case of glucose the temperature area over which we can calculate the osmotic pressure from the freezing point lowering is much smaller. In fact, only around 0° can it be calculated, because somewhere above 0° and below 10° the ratio of osmotic to gas pressure which was constant and abnormally high begins to decline, and then at 25° and 30°, where the ratio becomes constant and unity, the observed lowering of the freezing point no longer can be used in calculating the osmotic pressure of glucose solutions, but instead we must make use of the theoretical depression, that is, a molecular depression of 1.85.°

E. H. Loomis in his work on "The Freezing Points of Aqueous Solutions of Non-Electrolytes"[1] made a careful determination of the molecular depression of 0.1 to 0.5 weight-normal solutions of mannite, and found that they were normal 1.85°. Therefore, this fact makes the investigation of the osmotic pressure of mannite of especial interest. Substituting in formula 6, we find that the osmotic pressure as calculated from the freezing point lowering is normal, that is, equals the gas pressure for 0°. Now, from this and the relations which were found to hold between osmotic pressure and lowering of freezing points of glucose and cane-sugar solutions, we would say that the ratio of osmotic to gas pressures for mannite solutions would be unity for all temperatures.

[1]Zeit. Phys. Chemie., 32, p. 599.

The mannite was obtained from Germany in sufficient quantity and of a degree of purity that no further purification was necessary for its use in this investigation. Unfortunately, we were only able to work with 0.1 to 0.5 weight-normal solutions at 10°, 20° and 30° and 0.1 to 0.6 weight-normal solutions at 40° because of the limited solubility of the mannite.

All the solutions used in this investigation were made up on the weight-normal basis, that is, by dissolving a gram molecular weight, or decimal part thereof, of the solute in a 1000 grams of water. The true concentration of a solution, wherever the influence of the solvent upon the solute is involved, is determined by the numerical ratio of the molecules of the solute to those of the solvent, rather than by the number of solute molecules in a given space. Thus, by using the weight-normal basis of making up solutions we always have the same mass of the solvent coming into play, no matter what the concentration. Moreover, just as we must introduce a correction in the simple equation $p\,v = R\,T$ for gases for the volume occupied by the gaseous molecules, which we do by using Van der Waal's equation $(p + \frac{a}{v^2})(v - b) = K\,T$, so also we must introduce a similar correction in the equation for solutions $p\,(v - b) = K\,T$, in which b expresses the volume occupied by the solute molecules. Suppose we dissolve a gram molecular weight of the solute in water and dilute to a litre. The true volume would be $v - b = 1000$ c.c.$- b$, the volume of the solute molecules. If now, however, we take a gram molecular weight of the solute and dissolve in a 1000 grs. of water, in that mass of the solvent which has the unit volume 1 litre at the temperature of maximum density, and the volume here would be $v + b - b = V = 1000$ c.c. Thus, by using the weight-normal system of making up solutions, we may be supposed automatically to correct for the b in the equation $p\,(v - b) = K\,T$.

EXPERIMENTAL.

CELLS.

Of the cells which were used in this investigation on mannite, some were new, that is, had never before been set up for any measurement, while the others all had been used in measuring osmotic pressure, some with electrolytes, some with non-electrolytes.

The first step to be taken with the finished cell is to expel the air from the pores and to replace it by water. This is accomplished by means of "electrical endosmose," that is, by electrolyzing a dilute solution of lithium sulphate which nearly fills the cell and in which it is immersed to the lower edge of the glazed portion. The lithium ion carries with it the largest atmosphere of water and, therefore, gives a greater endosmose than any other cation. When it is judged that all the air has been removed from the porous wall, the cell is removed, rinsed with pure water, and allowed to soak for a time in distilled water, which is frequently renewed. Finally the electrolysis is repeated, the cell this time being filled with distilled water. When the conductivity, after frequent renewals of the water, has fallen nearly to that which is normal for distilled water itself, the cell is ready for the deposition of the membrane.

Tenth weight-normal solutions of copper sulphate and potassium ferrocyanide are employed, the copper sulphate in which the anode is set being outside the cell and the potassium ferrocyanide, together with the cathode, being inside. Thus, by means of the electric current the two ions which form the membrane are driven into the cell wall, thereby causing the membrane to become firmly packed and embedded in the pore mouths. Due to the fact that the membrane is readily attacked by dilute alkalie, during the deposition the cell is flushed out every two minutes with a fresh solution of potassium ferrocyanide. This membrane-forming process is allowed to run one hour, when the cell is removed, rinsed with distilled water, and allowed to soak several days in thymol water, when it is again treated as in the first instance. The resistance rises higher and higher on successive treatments until a permanent maximum is reached, when the membrane is ready for its first measurement. The new cells were started on June 4, 1913, and on February 4, 1914, were ready to be set up for the measurement of the osmotic pressure of mannite at 10°.

The cells when not in use were allowed to soak in thymol water, in the membrane-depositing baths, at the temperature at which they were to be used for measurements, and every other day the membrane-forming process was repeated for an hour. After an experiment is finished the cell is emptied, thoroughly

washed, and allowed to soak in thymol water several days, after which it is treated like the other cells.

Of the old cells, A_6, I_6, M_6, P_6, U_6 were never used with electrolytes.

C_6, F_6, K_6, N_6, T_6, W_6, Y_6, Z_6, B_6, G_6, H_6, O_6, Q_6, S_6 were all used at some time in the measurement of the osmotic pressure of lithium chloride. Of these fourteen cells, the last six, B_6 to S_6, had at one time a membrane of nickel ferrocyanide, but when work was started on mannite, this membrane was changed to copper ferrocyanide simply by depositing the copper membrane on top of that of nickel.

The effect of exposing a membrane to an electrolyte is to render it sluggish in its action. This is to be seen, first, in the long time consumed by the cells in coming to equilibrium, and, secondly, in the considerable thermometer effects which are shown in the rather large fluctuations in pressure from day to day.

Another reason for the slowness of the cells in coming to equilibrium might be in the fact that the pores of the cells, due to reburning, have shrunk in size and consequently the effective area of the membrane has diminished.

Perhaps mannite itself may have a specific action on the membrane, tending to retard the passage of solvent through it. In an experiment, cell B_6, which, with mannite, took twenty-six days to come to equilibrium, when afterwards set up with 1.0 weight-normal solution of glucose, reached equilibrium on the thirteenth day. But before we can pass a final opinion on this point more experimental work must be done. This question is an important one, and will be fully investigated at a later period.

The cells No. 1, No. 2, No. 3, No. 4, No. 5, No. 6 are interesting because they had their old membrane removed and a new one deposited. The old membranes were removed by treating with an alkaline tartrate and then electrolyzing with dilute nitric acid, after which the cells were reburned in the potter's kiln, the air removed, the cells were thoroughly soaked and the new membrane subsequently deposited in the usual manner. Usually not much success attends such a process, but here we were successful, as is evidenced by Table XII. Not only did cell No. 5 give a good measurement the first time it was set up, but it came to equilibrium on the fifteenth day, which is quite rapid for mannite.

MANOMETERS.

Of the manometers which were used in this work on mannite, nothing special need be said in addition to what has been discussed elsewhere.[1] Several manometers which during the summer had been calibrated in the usual way were filled and their volume and capillary depression determined in the fall, and thus two new ones were added to our supply to make up for loss which we suffered in consequence of breakage.

One decided improvement, however, should be mentioned, and this is a new type cone made entirely of glass which replaces the old cone of brass and Wood's metal. The cone is that part of the manometer which is fastened into the cell by means of a brass collar and nut. The old type brass cone has two holes passing entirely through it, one for the manometer tube and the other for the hollow needle, which is employed for preliminary adjustment of pressure, both of which (the manometer and the needle) are securely fastened in the cone by means of Wood's metal.[2] Now, due to the contractions and expansions which this Wood's metal suffers as the cone is used at different temperatures, there is a tendency in some cases for the cone to become leaky around the manometer tube, and consequently high pressures cannot be maintained. This necessitates the taking down of the cell and setting up again with a new manometer. This is the only part of the manometer which gives trouble, and especially is this liable to happen at higher temperatures.

But with the glass cone all this trouble is obviated. This consists of a short capillary tube and cone made from a single piece of glass. The capillary in the tube continues through the cone, while to one side of this a second opening takes the place of the hollow needle of the brass cone. Through this second opening runs a thin brass or platinum rod having a thread at one end and at the other a brass cap which holds a rubber washer in place against the opening at the bottom of the cone. Thus by means of a threaded cap which screws down on the threaded end of this rod, pressure can be brought to bear against the rubber washer, thereby effectually closing this second opening through the cone.

This whole arrangement is then fastened into a brass cap which fits the brass collar and nut arrangement, by means of

[1] Carnegie Publication 198.
[2] For full description see *Ibid.*, 198.

which the manometer is fastened into the cell, by litharge glycerine cement. To this cap is fastened a brass tube which fits around the glass capillary tube, increasing its strength and thereby preventing the liability of snapping off from the cone when the valuable manometer is sealed on. Altogether it is quite an improvement over the old cones, and has given the best results in every instance.

BATHS.

In our constant temperature baths we had a large volume of water and air which were kept in constant circulation over first a cooling surface and then a heating surface. The cooling surfaces were coils of pipe through which tap-water circulated, while the heating surfaces were enclosed incandescent lamps. The baths themselves were maintained in special rooms whose temperature could be regulated so that the daily fluctuations would be very slight. By these means we were able to maintain any temperature at which we were working to within several hundredths of a degree. For a full account and description of the baths and temperature regulation, see Carnegie Publication 198.

In these measurements on mannite we had no means of testing whether the solutions maintained perfectly their concentrations while in the cells. In the case of cane sugar and glucose this could easily be done, because by means of the polariscope slight changes in the concentration of the solutions could be detected and measured. However, now we have an instrument, the "interferometer," made by Zeiss for use with optically inactive substances, and when the final measurements are made on mannite use will be made of this. However, even without this proof there is no reason to doubt the present measurements of the osmotic pressure of mannite, because surely, if there were changes in concentration occurring in the cells the ratio of osmotic to gas pressures would not have been so nearly constant as they were found to be.

The following tables are a brief outline of some of the measurements which I made with the collaboration of Dr. Frazer, and for a more complete discussion of the work, consult Carnegie Publication 198.

MEASUREMENTS.

TABLE V.

0.1 WEIGHT-NORMAL SOLUTION AT 10°. CALCULATED GAS PRESSURE, 2.308.

Experiment 1. Cell F-7. Resistance of membrane, 1,100,000 ohms. Manometer, 60. Time setting up cell, January 30, 1914. Barometer during final record: Max., 1.009; Min., .995. Initial pressure, 3.393. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
83d day, 3.300	85th day, 3.317	87th day, 3.317
84th day, 3.310	86th day, 3.307	

Mean of all daily pressures, April 23-27 = 3.310 atms.
Mean barometric pressure, April 23-27 = 1.003 atms.
Mean osmotic pressure, April 23-27 = 2.307 atms.*

TABLE VI.

Experiment 2. Cell Z-7. Resistance of membrane, 1,100,000 ohms. Manometer, 61. Time setting up cell, January 30, 1914. Barometer during final record: Max., 1.000; Min., .972. Initial pressure, 3.135. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
30th day, 3.315	34th day, 3.311	37th day, 3.309
31st day, 3.308	35th day, 3.313	38th day, 3.309
32d day, 3.310	36th day, 3.311	39th day, 3.311
33d day, 3.315		

Mean of all daily pressures, Feb. 28-Mar. 9 = 3.311 atms.
Mean barometric pressure, Feb. 28-Mar. 9 = 0.989 atms.
Mean osmotic pressure, Feb. 28-Mar. 9 = 2.322 atms.
Mean osmotic pressure for experiments 1 and 2 = 2.314 atms.
Ratio osmotic to gas pressure = 1.002.

*This experiment is of especial interest, owing to the fact of the long interval of time (83 days) between the setting up and the coming to equilibrium of the cell. Nothing similar to this having ever been experienced with either glucose or cane sugar. In the near future a thorough investigation will be carried out to ascertain whether mannite has a retarding effect on the action of the membrane in allowing water to diffuse through.

TABLE VII.

0.2 Weight-Normal Solution at 10°. Calculated Gas Pressure, 4.616.

Experiment 1. Cell D-6. Resistance of membrane, 1,100,000 ohms. Manometer, 44. Time setting up cell, January 29, 1914. Barometer during final record: Max., 1.000; Min., .972. Initial pressure 5.685. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
31st day, 5.621	35th day, 5.598	38th day, 5.590
32d day, 5.596	36th day, 5.596	39th day, 5.594
33d day, 5.582	37th day, 5.613	40th day, 5.598
34th day, 5.591		

Mean of all daily pressures, Feb. 28-Mar. 9 = 5.599 atms.
Mean barometric pressure, Feb. 28-Mar. 9 = 0.989 atms.
Mean osmotic pressure, Feb. 28-Mar. 9 = 4.610 atms.
Ratio osmotic to gas pressure = .998.

TABLE VIII.

0.3 Weight-Normal Solution at 10°. Calculated Gas Pressure, 6.925.

Experiment 1. Cell J-6. Resistance of membrane, 1,100,000 ohms. Manometer, 34. Time setting up cell, January 29, 1914. Barometer during final record: Max., 1.008; Min., .987. Initial pressure, 8.063. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
57th day, 7.958	61st day, 7.956	65th day, 7.938
58th day, 7.958	62d day, 7.942	66th day, 7.926
59th day, 7.962	63d day, 7.958	67th day, 7.928
60th day, 7.960	64th day, 7.957	

Mean of all daily pressures, Mar. 26-April 6 = 7.949 atms.
Mean barometric pressure, Mar. 26-April 6 = 0.999 atms.
Mean osmotic pressure, Mar. 26-April 6 = 6.950 atms.

TABLE IX.

Experiment 2. Cell P-6. Resistance of membrane 366,666 ohms. Manometer, 32. Time setting up cell, March 8, 1914. Barometer during final record: Max., 1.009; Min., .995. Initial pressure 8.768. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
46th day, 7.916	48th day, 7.944	50th day, 7.946
47th day, 7.932	49th day, 7.929	

Mean of all daily pressures, April 23-27 = 7.933 atms.
Mean barometric pressure, April 23-27 = 1.003 atms.
Mean osmotic pressure, April 23-27 = 6.930 atms.
Mean osmotic pressure for experiments 1 and 2 = 6.940 atms.
Ratio of osmotic to gas pressure = 1.002.

TABLE X.

0.4 Weight-Normal Solution at 10°. Calculated Gas Pressure, 9.233.

Experiment 1. Cell A-6. Resistance of membrane, 550,000 ohms. Manometer, 32. Time setting up cell, January 28, 1914. Barometer during final record: Max., 1,006; Min., .972. Initial pressure, 9.759. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
31st day, 10.297	35th day, 10.198	39th day, 10.173
32d day, 10.229	36th day, 10.155	40th day, 10.179
33d day, 10.160	37th day, 10.175	41st day, 10.206
34th day, 10.156	38th day, 10.186	

Mean of all daily pressures, Feb. 27-Mar. 9 = 10.192 atms.
Mean barometric pressure, Feb. 27-Mar. 9 = 0.991 atms.
Mean osmotic pressure, Feb. 27-Mar. 9 = 9.201 atms.

TABLE XI.

Experiment 2. Cell U-6. Resistance of membrane, 550,000 ohms. Manometer, 37. Time setting up cell, January 28, 1914. Barometer during final record: Max., 1.008; Min., .972. Initial pressure, 10.025. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
30th day, 10.318	34th day, 10.159	38th day, 10.202
31st day, 10.336	35th day, 10.195	39th day, 10.169
32d day, 10.207	36th day, 10.188	40th day, 10.173
33d day, 10.148	37th day, 10.188	41st day, 10.209

Mean of all daily pressures, Feb. 26-Mar. 9 = 10.208 atms.
Mean barometric pressure, Feb. 26-Mar. 9 = 0.992 atms.
Mean osmotic pressure, Feb. 26-Mar. 9 = 9.216 atms.
Mean osmotic pressure for experiments 1 and 2 = 9.208 atms.
Ratio of osmotic to gas pressure = .997.

TABLE XII.

0.5 WEIGHT-NORMAL SOLUTION AT 10°. CALCULATED GAS PRESSURE, 11.541.

Experiment 1. Cell No. 5. Resistance of membrane, 1,100,000 ohms. Manometer, 35. Time setting up cell, March 1, 1914. Barometer during final record: Max., 1.015; Min., .983. Initial pressure, 12.426. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
15th day, 12.622	19th day, 12.600	22d day, 12.627
16th day, 12.615	20th day, 12.626	23d day, 12.612
17th day, 12.600	21st day, 12.635	24th day, 12.622
18th day, 12.587		

Mean of all daily pressures, Mar. 15-24 = 12.614 atms.
Mean barometric pressure, Mar. 15-24 = 1.002 atms.
Mean osmotic pressure, Mar. 15-24 = 11.612 atms.
Ratio osmotic to gas pressure = 1.006.

TABLE XIII.

0.1 Weight-Normal Solution at 20°. Calculated Gas Pressure, 2.390.

Experiment 1. Cell U-6. Resistance of membrane, 366,666 ohms. Manometer, 61. Time setting up cell, December 17, 1913. Barometer during final record: Max., 1.017; Min., .978. Initial pressure, 3.443. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
20th day, 3.406	24th day, 3.376	28th day, 3.388
21st day, 3.400	25th day, 3.376	29th day, 3.389
22d day, 3.396	26th day, 3.380	30th day, 3.384
23d day, 3.377	27th day, 3.380	

Mean of all daily pressures, Jan. 5-15 = 3.387 atms.
Mean barometric pressure, Jan. 5-15 = 0.996 atms.
Mean osmotic pressure, Jan. 5-15 = 2.391 atms.

TABLE XIV.

Experiment 2. Cell I-6. Resistance of membrane, 157,142 ohms. Manometer, 61. Time setting up cell, January 15, 1914. Barometer during final record: Max., 1.008; Min., .982. Initial pressure, 3.386. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
2d day, 3.386	5th day, 3.416	8th day, 3.358
3d day, 3.367	6th day, 3.395	9th day, 3.399
4th day, 3.446	7th day, 3.373	10th day, 3.386

Mean of all daily pressures, Jan. 16-24 = 3.391 atms.
Mean barometric pressure, Jan. 16-24 = 0.994 atms.
Mean osmotic pressure, Jan. 16-24 = 2.397 atms.
Mean osmotic pressure for experiments 1 and 2 = 2.394 atms.
Ratio of osmotic to gas pressure = 1.001.

TABLE XV.

0.2 Weight-Normal Solution at 20°. Calculated Gas Pressure, 4.780.

Experiment 1. Cell M-6. Resistance of membrane, 550,000 ohms. Manometer, 34. Time setting up cell, December 17, 1913. Barometer during final record: Max., 1.005; Min., .978. Initial pressure, 5.866. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
14th day, 5.822	18th day, 5.769	22d day, 5.746
15th day, 5.806	19th day, 5.759	23d day, 5.764
16th day, 5.797	20th day, 5.756	24th day, 5.754
17th day, 5.780	21st day, 5.743	

Mean of all daily pressures, Dec. 30-Jan. 9 = 5.722 atms.
Mean barometric pressure, Dec. 30-Jan. 9 = 0.994 atms.
Mean osmotic pressure, Dec. 30-Jan. 9 = 4.778 atms.

TABLE XVI.

Experiment 2. Cell P-6. Resistance of membrane, 366,666 ohms. Manometer, 34. Time setting up cell, January 9, 1914. Barometer during final record: Max., 1.017; Min., .982. Initial pressure, 5.908. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
4th day, 5.812	8th day, 5.766	12th day, 5.774
5th day, 5.801	9th day, 5.757	13th day, 5.764
6th day, 5.792	10th day, 5.782	14th day, 5.765
7th day, 5.781	11th day, 5.786	

Mean of all daily pressures, Jan. 12-22 = 5.780 atms.
Mean barometric pressure, Jan. 12-22 = 0.997 atms.
Mean osmotic pressure, Jan. 12-22 = 4.783 atms.
Mean osmotic pressure for experiments 1 and 2 = 4.780 atms.
Ratio of osmotic to gas pressure = 1.000.

TABLE XVII.

0.3 Weight-Normal Solution at 20°. Calculated Gas Pressure, 7.170.

Experiment 1. Cell O-6. Resistance of membrane, 366,666 ohms. Manometer, 32. Time setting up cell, November 29, 1913. Barometer during final record: Max., 1.009; Min., .981. Initial pressure, 8.584. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
30th day, 8.288	34th day, 8.156	37th day, 8.147
31st day, 8.170	35th day, 8.152	38th day, 8.140
32d day, 8.175	36th day, 8.150	39th day, 8.128
33d day, 8.167		

Mean of all daily pressures, Dec. 28-Jan. 6 = 8.167 atms.
Mean barometric pressure, Dec. 28-Jan. 6 = 0.998 atms.
Mean osmotic pressure, Dec. 28-Jan. 6 = 7.169 atms.

TABLE XVIII.

Experiment 2. Cell G-6. Resistance of membrane, 275,000 ohms. Manometer, 35. Time setting up cell, November 29, 1913. Barometer during final record: Max., 1.007; Min., .992. Initial pressure, 7.743. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
18th day, 8.235	22d day, 8.168	25th day, 8.212
19th day, 8.195	23d day, 8.144	26th day, 8.221
20th day, 8.132	24th day, 8.209	27th day, 8.184
21st day, 8.222		

Mean of all daily pressures, Dec. 16-25 = 8.192 atms.
Mean barometric pressure, Dec. 16-25 = 0.999 atms.
Mean osmotic pressure, Dec. 16-25 = 7.193 atms.
Mean osmotic pressure for experiments 1 and 2 = 7.181 atms.
Ratio of osmotic to gas pressure = 1.001.

TABLE XIX.

0.4 Weight-Normal Solution at 20°. Calculated Gas Pressure, 9.560.

Experiment 1. Cell C-6. Resistance of membrane, 550,000 ohms. Manometer, 34. Time setting up cell, October 30, 1913. Barometer during final record: Max., 1.011; Min., .984. Initial pressure, 11.378. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
12th day, 10.634	16th day, 10.597	20th day, 10.594
13th day, 10.661	17th day, 10.578	21st day, 10.630
14th day, 10.638	18th day, 10.575	22d day, 10.639
15th day, 10.624	19th day, 10.553	23d day, 10.647

Mean of all daily pressures, Nov. 10-21 = 1.614 atms.
Mean barometric pressure, Nov. 10-21 = 1.001 atms.
Mean osmotic pressure, Nov. 10-21 = 9.613 atms.

TABLE XX.

Experiment 2. Cell Q-6. Resistance of membrane, 550,000 ohms. Manometer, 41. Time setting up cell, December 3, 1913. Barometer during final record: Max., 1.011; Min., .985. Initial pressure, 9.171. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
5th day, 10.571	9th day, 10.550	12th day, 10.598
6th day, 10.541	10th day, 10.546	13th day, 10.616
7th day, 10.545	11th day, 10.578	14th day, 10.634
8th day, 10.551		

Mean of all daily pressures, Dec. 7-16 = 10.573 atms.
Mean barometric pressure, Dec. 7-16 = 1.001 atms.
Mean osmotic pressure, Dec. 7-16 = 9.572 atms.

TABLE XXI.

Experiment 3. Cell H-6. Resistance of membrane, 366.666 ohms. Manometer, 40. Time setting up cell, December 2, 1913. Barometer during final record: Max., 1.005; Min., .982. Initial pressure, 8.464. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
28th day, 10.451	32d day, 10.539	35th day, 10.542
29th day, 10.483	33d day, 10.537	36th day, 10.546
30th day, 10.509	34th day, 10.544	37th day, 10.549
31st day, 10.513		

Mean of all daily pressures, Dec. 29-Jan. 7 = 10.521 atms.
Mean barometric pressure, Dec. 29-Jan 7 = 0.997 atms.
Mean osmotic pressure, Dec. 29-Jan. 7 = 9.524 atms.
Mean osmotic pressure for experiments 1, 2 and 3 = 9.569 atms.
Ratio of osmotic to gas pressure = 1.001.

TABLE XXII.

0.5 WEIGHT-NORMAL SOLUTION AT 20°. CALCULATED GAS PRESSURE, 11.950.

Experiment 1. Cell O-6. Resistance of membrane, 1,100,000 ohms. Manometer, 35. Time setting up cell, October 29, 1913. Barometer during final record: Max., 1.011; Min., .965. Initial pressure, 11.652. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
12th day, 12.944	17th day, 12.956	21st day, 12.911
13th day, 12.945	18th day, 12.897	22d day, 12.946
14th day, 12.916	19th day, 12.892	23d day, 12.963
15th day, 12.921	20th day, 12.873	24th day, 12.971
16th day, 12.910		

Mean of all daily pressures, Nov. 9-21 = 12.927 atms.
Mean barometric pressure, Nov. 9-21 = 0.998 atms.
Mean osmotic pressure, Nov. 9-21 = 11.929 atms.

TABLE XXIII.

Experiment 2. Cell S-6. Resistance of membrane, 366,666 ohms. Manometer, 36. Time setting up cell, November 17, 1913. Barometer during final record: Max., 1.013; Min., .985. Initial pressure, 14.671. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
14th day, 13.017	18th day, 12.990	21st day, 12.980
15th day, 12.989	19th day, 12.995	22d day, 12.965
16th day, 13.002	20th day, 13.007	23d day, 12.983
17th day, 12.993		

Mean of all daily pressures, Nov. 30-Dec. 9 = 12.992 atms.
Mean barometric pressure, Nov. 30-Dec. 9 = 1.001 atms.
Mean osmotic pressure, Nov. 30-Dec. 9 = 11.991 atms.
Mean osmotic pressure for experiments 1 and 2 = 11.960 atms.
Ratio of osmotic to gas pressure = 1.001.

TABLE XXIV.

0.1 WEIGHT-NORMAL SOLUTION AT 30°. CALCULATED GAS PRESSURE, 2.472.

Experiment 1. Cell O-6. Resistance of membrane, 550,000 ohms. Manometer, 11. Time setting up cell March 17, 1913. Barometer during final record: Max., 1,014; Min., .997. Initial pressure, 3.736. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
17th day, 3.530	21st day, 3.476	25th day, 3.461
18th day, 3.519	22d day, 3.470	26th day, 3.455
19th day, 3.531	23d day, 3.468	27th day, 3.450
20th day, 3.499	24th day, 3.465	

Mean of all daily pressures, April 2-12 = 3.484 atms.
Mean barometric pressure, April 2-12 = 1.005 atms.
Mean osmotic pressure, April 2-12 = 2.479 atms.

TABLE XXV.

Experiment 2. Cell Q-6. Resistance of membrane, 366,666 ohms. Manometer, 9. Time setting up cell, April 30, 1913. Barometer during final record: Max., 1.004; Min., .990. Initial pressure, 3.790. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
20th day, 3.415	23d day, 3.481	26th day, 3.467
21st day, 3.422	24th day, 3.431	27th day, 3.438
22d day, 3.414	25th day, 3.512	28th day, 3.507

Mean of all daily pressures, May 19-28 = 3.454 atms.
Mean barometric pressure, May 19-28 = 0.996 atms.
Mean osmotic pressure, May 19-28 = 2.458 atms.
Mean osmotic pressure for experiments 1 and 2 = 2.469 atms.
Ratio of osmotic to gas pressure = .999.

TABLE XXVI.

0.2 WEIGHT-NORMAL SOLUTION AT 30°. CALCULATED GAS PRESSURE, 4.943.

Experiment 1. Cell K-6. Resistance of membrane, 122,222 ohms. Manometer, 32. Time setting up cell, February 19, 1913. Barometer during final record: Max., 1.027; Min., .977. Initial pressure, 6.943. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
28th day, 5.996	32d day, 5.946	36th day, 5.941
29th day, 5.958	33d day, 5.947	37th day, 5.936
30th day, 5.952	34th day, 5.944	38th day, 5.956
31st day, 5.951	35th day, 5.942	39th day, 5.955

Mean of all daily pressures, March 18-29 = 5.952 atms.
Mean barometric pressure, March 18-29 = 1.006 atms.
Mean osmotic pressure, March 18-29 = 4.946 atms.

TABLE XXVII.

Experiment 2. Cell O-6. Resistance of membrane, 110,000 ohms. Manometer, 32. Time setting up cell, April 16, 1913. Barometer during final record: Max., 1.004; Min., .992. Initial pressure, 7.409. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
29th day, 5.966	33d day, 5.945	36th day, 5.952
30th day, 5.922	34th day, 5.967	37th day, 5.915
31st day, 5.916	35th day, 5.939	38th day, 5.907
32d day, 5.950		

Mean of all daily pressures, May 14-23 = 5.938 atms.
Mean barometric pressure, May 14-23 = 0.998 atms.
Mean osmotic pressure, May 14-23 = 4.940 atms.
Mean osmotic pressure for experiments 1 and 2 = 4.943 atms.
Ratio of osmotic to gas pressure = 1.000.

TABLE XXVIII.

0.3 WEIGHT-NORMAL SOLUTION AT 30°. CALCULATED GAS PRESSURE, 7.415.

Experiment 1. Cell H-6. Resistance of membrane, 550,000 ohms. Manometer, 44. Time setting up cell, January 24, 1913. Barometer during final record: Max., 1.009; Min., .987. Initial pressure, 12.657. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
23d day, 8.440	28th day, 8.456	32d day, 8.435
24th day, 8.429	29th day, 8.474	33d day, 8.443
25th day, 8.440	30th day, 8.334	34th day, 8.437
26th day, 8.446	31st day, 8.381	35th day, 8.434
27th day, 8.445		

Mean of all daily pressures, Feb. 15-28 = 8.432 atms.
Mean barometric pressure, Feb. 15-28 = 0.998 atms.
Mean osmotic pressure, Feb. 15-28 = 7.434 atms.

TABLE XXIX.

Experiment 2. Cell G-6. Resistance of membrane, 366,666 ohms. Manometer, 37. Time setting up cell, February 13, 1913. Barometer during final record: Max., 1.011; Min., .986. Initial pressure, 9.196. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
20th day, 8.449	24th day, 8.429	27th day, 8.411
21st day, 8.444	25th day, 8.424	28th day, 8.416
22d day, 8.435	26th day, 8.419	29th day, 8.413
23d day, 8.438		

Mean of all daily pressures, Mar. 4-14 = 8.428 atms.
Mean barometric pressure, Mar. 4-14 = 1.002 atms.
Mean osmotic pressure, Mar. 4-14 = 7.426 atms.
Mean osmotic pressure for experiments 1 and 2 = 7.430 atms.
Ratio of osmotic to gas pressure = 1.002.

TABLE XXX.

0.4 WEIGHT-NORMAL SOLUTION AT 30°. CALCULATED GAS PRESSURE, 9.886.

Experiment 1. Cell B-6. Resistance of membrane, 1,100,000 ohms. Manometer, 32. Time setting up cell, January 17, 1913. Barometer during final record: Max., 1.018; Min., .982. Initial pressure, 12,692. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
11th day, 10.880	15th day, 10.779	19th day, 10.749
12th day, 10.883	16th day, 10.782	20th day, 10.753
13th day, 10.855	17th day, 10.773	21st day, 10.738
14th day, 10.818	18th day, 10.719	22d day, 10.732

Mean of all daily pressures, Jan. 27-Feb. 7 = 10.800 atms.
Mean barometric pressure, Jan. 27-Feb. 7 = 0.997 atms.
Mean osmotic pressure, Jan. 27-Feb. 7 = 9.803 atms.

TABLE XXXI.

Experiment 2. Cell Q-6. Resistance of membrane, 275,000 ohms. Manometer, 30. Time setting up cell, January 20, 1913. Barometer during final record: Max., 1.018; Min., .982. Initial pressure, 11,550. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
7th day, 10.990	12th day, 10.938	16th day, 10.928
8th day, 10.964	13th day, 10.944	17th day, 10.919
9th day, 10.968	14th day, 10.949	18th day, 10.923
10th day, 10.967	15th day, 10.911	19th day, 10.919
11th day, 10.953		

Mean of all daily pressures, Jan. 26-Feb. 7 = 10.946 atms.
Mean barometric pressure, Jan 26-Feb. 7 = 0.997 atms.
Mean osmotic pressure, Jan. 26-Feb. 7 = 9.949 atms.

TABLE XXXII.

Experiment 3. Cell S-6. Resistance of membrane, 550,000 ohms. Manometer, 36. Time setting up cell, April 16, 1913. Barometer during final record: Max., 1.000; Min., .989. Initial pressure, 12.623. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
38th day, 10.929	41st day, 10.985	44th day, 10.825
39th day, 10.891	42d day, 10.817	45th day, 10.823
40th day, 10.966	43d day, 10.812	46th day, 10.822

Mean of all daily pressures, May 23-31 = 10.875 atms.
Mean barometric pressure, May 23-31 = 0.993 atms.
Mean osmotic pressure, May 23-31 = 9.882 atms.
Mean osmotic pressure for experiments 1, 2 and 3 = 9.878 atms.
Ratio of osmotic to gas pressure = .999.

TABLE XXXIII.

0.5 Weight-Normal Solution at 30°. Calculated Gas Pressure, 12.358.

Experiment 1. Cell G-6. Resistance of membrane, 550,000 ohms. Manometer, 34. Time setting up cell, March 19, 1913. Barometer during final record: Max., 1,016; Min., .985. Initial pressure, 11.187. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
31st day, 13.383	36th day, 13.255	40th day, 13.275
32d day, 13.346	37th day, 13.220	41st day, 13.270
33d day, 13.376	38th day, 13.209	42d day, 13.307
34th day, 13.392	39th day, 13.336	43d day, 13.319
35th day, 13.544		

Mean of all daily pressures, April 18-May 1 = 13.326 atms.
Mean barometric pressure, April 18-May 1 = 1.000 atms.
Mean osmotic pressure, April 18-May 1 = 12.326 atms.

TABLE XXXIV.

Experiment 2. Cell C-6. Resistance of membrane, 275,000 ohms. Manometer, 37. Time setting up cell, April 16, 1913. Barometer during final record: Max., 1.008; Min., .993. Initial pressure, 14.598. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
16th day, 13.406	21st day, 13.361	25th day, 13.530
17th day, 13.321	22d day, 13.437	26th day, 13.385
18th day, 13.251	23d day, 13.423	27th day, 13.367
19th day, 13.311	24th day, 13.400	28th day, 13.279
20th day, 13.272		

Mean of all daily pressures, May 1-14 = 13.365 atms.
Mean barometric pressure, May 1-14 = 1.001 atms.
Mean osmotic pressure, May 1-14 = 12.364 atms.
Mean osmotic pressure for experiments 1 and 2 = 12.345 atms.
Ratio of osmotic to gas pressure = .998.

TABLE XXXV.

0.1 Weight-Normal Solution at 40°. Calculated Gas Pressure, 2.553.

Experiment 1. Cell S-6. Resistance of membrane, 275,000 ohms. Manometer, 61. Time setting up cell, March 14, 1914. Barometer during final record: Max., 1.004; Min., .986. Initial pressure, 3.160. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
35th day, 3.563	37th day, 3.550	39th day, 3.551
36th day, 3.560	38th day, 3.544	

Mean of all daily pressures, April 17-21 = 3.554 atms.
Mean barometric pressure, April 17-21 = 0.997 atms.
Mean osmotic pressure, April 17-21 = 2.557 atms.
Ratio of osmotic to gas pressure = 1.001.

TABLE XXXVI.

0.2 Weight-Normal Solution at 40°. Calculated Gas Pressure, 5.107.

Experiment 1. Cell O-6. Resistance of membrane, 366,666 ohms. Manometer, 37. Time setting up cell, March 16, 1914. Barometer during final record: Max., 1.006; Min., .985. Initial pressure, 6.327. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
22d day, 6.157	26th day, 6.094	29th day, 6.070
23d day, 6.143	27th day, 6.095	30th day, 6.082
24th day, 6.116	28th day, 6.078	31st day, 6.077
25th day, 6.093		

Mean of all daily pressures, April 6-15 = 6.101 atms.
Mean barometric pressure, April 6-15 = 0.998 atms.
Mean osmotic pressure, April 6-15 = 5.103 atms.

TABLE XXXVII.

Experiment 2. Cell Q-6. Resistance of membrane, 157,142 ohms. Manometer, 40. Time setting up cell, March 16, 1914. Barometer during final record: Max., 1.011; Min., .985. Initial pressure, 5.992. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
12th day, 6.155	17th day, 6.091	21st day, 6.122
13th day, 6.148	18th day, 6.078	22d day, 6.111
14th day, 6.134	19th day, 6.110	23d day, 6.091
15th day, 6.132	20th day, 6.105	24th day, 6.056
16th day, 6.101		

Mean of all daily pressures, Mar. 27-April 8 = 6.110 atms.
Mean barometric pressure, Mar. 27-April 8 = 0.999 atms.
Mean osmotic pressure, Mar. 27-April 8 = 5.111 atms.
Mean osmotic pressure for experiments 1 and 2 = 5.107 atms.
Ratio of osmotic to gas pressure = 1.000.

TABLE XXXVIII.

0.3 WEIGHT-NORMAL SOLUTION AT 40°. CALCULATED GAS PRESSURE, 7.660.

Experiment 1. Cell C-6. Resistance of membrane, 110,000 ohms. Manometer, 44. Time setting up cell, December 3, 1913. Barometer during final record: Max., 1.017; Min., .988. Initial pressure, 8.211. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
40th day, 8.606	43d day, 8.671	46th day, 8.715
41st day, 8.640	44th day, 8.652	47th day, 8.719
42d day, 8.677	45th day, 8.644	48th day, 8.668

Mean of all daily pressures, Jan. 11-19 = 8.663 atms.
Mean barometric pressure, Jan. 11-19 = 0.999 atms.
Mean osmotic pressure, Jan. 11-19 = 7.664 atms.

TABLE XXXIX.

Experiment 2. Cell T-6. Resistance of membrane, 84,615 ohms. Manometer, 43. Time setting up cell, April 21, 1914. Barometer during final record: Max., 1.002; Min., .982. Initial pressure, 11,428. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
10th day, 8.727	13th day, 8.659	15th day, 8.609
11th day, 8.723	14th day, 8.638	16th day, 8.592
12th day, 8.665		

Mean of all daily pressures, April 30-May 6 = 8.659 atms.
Mean barometric pressure, April 30-May 6 = 0.995 atms.
Mean osmotic pressure, April 30-May 6 = 7.664 atms.
Mean osmotic pressure for experiments 1 and 2 = 7.664 atms.
Ratio of osmotic to gas pressure = 1.000.

TABLE XL.

0.4 WEIGHT-NORMAL SOLUTION AT 40°. CALCULATED GAS PRESSURE, 10.213.

Experiment 1. Cell F-6. Resistance of membrane, 55,000 ohms. Manometer, 37. Time setting up cell, December 17, 1913. Barometer during final record: Max., 1,005; Min., .982. Initial pressure, 11.909. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
15th day, 11.249	19th day, 11.163	22d day, 11.168
16th day, 11.227	20th day, 11.123	23d day, 11.136
17th day, 11.169	21st day, 11.158	24th day, 11.256
18th day, 11.291		

Mean of all daily pressures, Dec. 31-Jan. 9 = 11.194 atms.
Mean barometric pressure, Dec. 31-Jan. 9 = 0.993 atms.
Mean osmotic pressure, Dec. 31-Jan. 9 = 10.201 atms.

TABLE XLI.

Experiment 2. Cell C-6. Resistance of membrane, 110,000 ohms. Manometer, 41. Time setting up cell, February 7, 1914. Barometer during final record: Max., 1.011; Min., .985. Initial pressure, 18.856. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
53d day, 11.287	56th day, 11.238	59th day, 11.215
54th day, 11.279	57th day, 11.237	60th day, 11.188
55th day, 11.241	58th day, 11.221	61st day, 11.150

Mean of all daily pressures, Mar. 31-April 8 = 11.228 atms.
Mean barometric pressure, Mar. 31-April 8 = 0.998 atms.
Mean osmotic pressure, Mar. 31-April 8 = 10.230 atms.
Mean osmotic pressure for experiments 1 and 2 = 10.215 atms.
Ratio of osmotic to gas pressure = 1.000.

TABLE XLII.

0.5 WEIGHT-NORMAL SOLUTION AT 40°. CALCULATED GAS PRESSURE, 12.767.

Experiment 1. Cell K-6. Resistance of membrane, 57,894 ohms. Manometer, 41. Time setting up cell, December 16, 1913. Barometer during final record: Max., 1.017; Min., .987. Initial pressure, 13.351. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
26th day, 13.669	30th day, 13.858	33d day, 13.773
27th day, 13.601	31st day, 13.866	34th day, 13.874
28th day, 13.668	32d day, 13.853	35th day, 13.852
29th day, 13.887		

Mean of all daily pressures, Jan. 10-19 = 13.790 atms.
Mean barometric pressure, Jan. 10-19 = 0.998 atms.
Mean osmotic pressure, Jan. 10-19 = 12.792 atms.

TABLE XLIII.

Experiment 2. Cell F-6. Resistance of membrane, 55,000 ohms. Manometer, 30. Time setting up cell, February 7, 1914. Barometer during final record: Max., 1.006; Min., .988. Initial pressure, 19.623. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
28th day, 13.755	32d day, 13.830	36th day, 13.832
29th day, 13.775	33d day, 13.844	37th day, 13.842
30th day, 13.762	34th day, 13.830	38th day, 13.816
31st day, 13.812	35th day, 13.853	

Mean of all daily pressures, Mar. 6-16 = 13.814 atms.
Mean barometric pressure, Mar. 6-16 = 0.998 atms.
Mean osmotic pressure, Mar. 6-16 = 12.816 atms.
Mean osmotic pressure for experiments 1 and 2 = 12.804 atms.
Ratio of osmotic to gas pressure = 1.002.

TABLE XLIV.

0.6 WEIGHT-NORMAL SOLUTION AT 40°. CALCULATED GAS PRESSURE, 15.320.

Experiment 1. Cell B-6. Resistance of membrane, 91,666 ohms. Manometer, 42. Time setting up cell, January 9, 1914. Barometer during final record: Max., 1.019; Min., .977. Initial pressure, 15.062. Observed mean daily total pressures after cell became constant.

FINAL RECORD.

Atms.	Atms.	Atms.
26th day, 16.457	30th day, 16.236	34th day, 16.331
27th day, 16.290	31st day, 16.270	35th day, 16.253
28th day, 16.290	32d day, 16.456	36th day, 16.328
29th day, 16.285	33d day, 13.364	

Mean of all daily pressures, Feb. 3-13 = 16.324 atms.
Mean barometric pressure, Feb. 3-13 = 1.005 atms.
Mean osmotic pressure, Feb. 3-13 = 15.319 atms.
Ratio of osmotic to gas pressure = 1.000.

TABLE XLV.

WEIGHT-NORMAL CONCENTRATION.

	0.1	0.2	0.3	0.4	0.5	0.6
Temp.		*Mean Osmotic Pressures in Atmospheres.*				
10°	2.314	4.610	6.940	9.208	11.614	------
20°	2.394	4.780	7.181	9.569	11.960	------
30°	2.469	4.943	7.430	9.878	12.345	------
40°	2.557	5.107	7.664	10.215	12.804	15.319

TABLE XLVI.

WEIGHT-NORMAL CONCENTRATION.

	0.1	0.2	0.3	0.4	0.5	0.6
Temp.		*Ratio of Osmotic to Gas Pressure.*				
10°	1.002	0.998	1.002	0.997	1.006	-----
20°	1.001	1.000	1.001	1.001	1.001	-----
30°	0.999	1.000	1.002	0.999	0.998	-----
40°	1.001	1.000	1.000	1.000	1.002	1.000

DISCUSSION OF MEASUREMENTS.

Tables V to XLIV give a somewhat detailed account of each experiment.

Table XLV gives for each of the concentrations with which it was possible to work the osmotic pressures, which have been found at 10°, 20°, 30°, and 40°.

Table XLVI shows the ratio of the osmotic pressures given in Table XLV to the calculated gas pressures of the solute.

CONCLUSIONS.

The conclusions which can be drawn from Table XLVI are:

1. In all solutions of mannite from 0.1 to 0.6 weight-normal the ratio of the observed osmotic to the estimated gas pressure of the solute is constant and unity for each concentration at 10°, 20°, 30°, and 40°. This proves, therefore, that between the specified limits of concentration and temperature the osmotic pressure of mannite solutions obeys both the laws of Gay-Lussac and of Boyle for gases.

2. If a substance exhibits a normal molecular depression of the freezing point it appears probable from the experience with mannite that the ratio of osmotic to gas pressures will be unity at all temperatures. In other words, that the osmotic pressure of its solutions will obey the laws of Gay-Lussac and of Boyle for gases.

3. By use of the weight-normal system of making up solutions the equation $p\ (v - b) = K\,T$, in which we may be supposed automatically to correct for the b, holds not only for dilute, but also for more concentrated solutions. Stated in another way, the equation of Van't Hoff *for very dilute solutions* ($pv = KT$) appears to hold also for concentrated solutions of mannite, if we allow the v to signify not the volume of the solution, but that of the free solvent.

The osmotic pressure of solutions of mannite will be next determined at 0°, also at temperatures as much above 40° as it is practicable to work. This will be done in order to ascertain whether substances exhibiting normal depressions of the freezing points may be expected to exhibit osmotic pressures conforming under all circumstances to the gas laws.

BIOGRAPHY.

Edwin Louis Frederick was born March 17, 1891, at Baltimore, Md. His early education was obtained at the public schools of that city, graduating from the Baltimore City College in the spring of 1907. In the fall of that year he entered The Johns Hopkins University, Baltimore, Md., and graduated in 1911, receiving the degree of Bachelor of Arts. October, 1911, he entered the graduate department of this university, majoring in Chemistry, with Physical Chemistry and Applied Geology, respectively, as his first and second subordinate subjects.

In 1911-1912 he was laboratory assistant, while in 1912-1913 he held a Hopkins scholarship, and in June, 1913, was appointed a University Fellow for the year 1913-1914.

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